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Hydroxyethylcellulose

68.1	Introduction	68-1
68.2	Chemical Composition of Hydroxyethylcellulose	68-2
68.3	Types and Grades of Hydroxyethylcellulose.....	68-2
68.4	Chemical and Physical Properties of Hydroxyethylcellulose	68-3
68.5	Incorporating Hydroxyethylcellulose into Latex Paints	68-3
68.6	Application Properties of Latex Paints Thickened with Hydroxyethylcellulose.....	68-4
	Leveling and Sag Resistance • Film Build • Spatter Resistance	
	Reference	68-5

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68.1 Introduction

Hydroxyethylcellulose (HEC) is a nonionic, water-soluble polymer derived from cellulose. It is used in water-borne paints for its action as a thickener, stabilizer, and/or suspending agent. HEC not only imparts mechanical and chemical stability to the paint system, it plays a significant role in controlling the rheology of the paint during manufacture, storage, and application. HEC is the most commonly used thickener in latex paints. In fact, it is often referred to as the industry standard for thickening.

Physically, hydroxyethylcellulose is a white, free-flowing powder that dissolves readily in hot or cold water. Available in a variety of types and grades, it can be used to produce aqueous solutions with a wide range of viscosities and a pseudoplastic nature. Upon drying, solutions of HEC form clear, gel-free films.

The nonionic nature of HEC is an advantage in latex paints. Nonionics can be used over a wide pH range and, unlike polyelectrolytes, are compatible with salts and charged species such as surfactants, latex particles, and colorants.

More recently, a hydrophobically modified hydroxyethylcellulose (HMHEC) was introduced to the latex paint industry.¹ HMHEC is an associative cellulosic polymer designed specifically for use in latex paints. It is a nonionic water-soluble polymer that contains both hydroxyethyl and long chain alkyl groups. This unique dual substitution differentiates the new-generation rheological modifier from traditional HEC. Like HEC, hydrophobically modified hydroxyethylcellulose thickens the aqueous phase of the paint, but substantial viscosity is built through association of the polymer's hydroprobes with the paint components. HMHEC combines the desirable properties of HEC with the enhanced rheology control (particularly with respect to spatter resistance and film build) required for today's coatings. A detailed discussion of HMHEC's chemical composition and rheological performance in latex paints is provided by Shaw and Leipold.

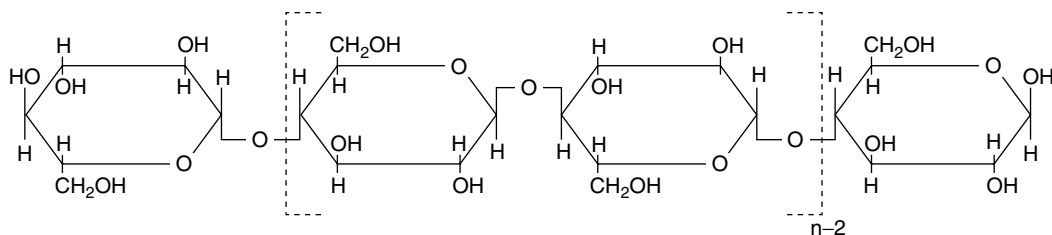


FIGURE 68.1 Structure of cellulose.

68.2 Chemical Composition of Hydroxyethylcellulose

The cellulose molecule is a polymeric chain composed of repeating anhydroglucose units (Figure 68.1). There is considerable intrachain and interchain hydrogen bonding, which results in a highly ordered, highly crystalline structure. It is for this reason that cellulose is not soluble in water.

The reactions used to make derivations of cellulose are straightforward. Cellulose is reacted with alkali, such as sodium hydroxide, to form alkali cellulose. The alkali treatment is necessary to disrupt the cellulose crystallinity. The swollen chain is then ready for the addition of appropriate substituents. Substitution on the cellulose chain causes disorder and forces the chains apart so that water may enter and solvate the chain. Each anhydroglucose unit in the cellulose molecule has three reactive hydroxyl groups. The number of hydroxyl groups substituted in any reaction is known as the degree of substitution (DS). Technically, all three hydroxyls can be substituted. The product from such a reaction would have a DS of 3.

Hydroxyethyl groups can be introduced into the cellulose molecule in two ways. First, ethylene oxide reacts with the hydroxyls in the cellulose chain. Second, ethylene oxide, reacting with previously substituted hydroxyls, can polymerize to form a side chain.

The average number of moles of ethylene oxide that attach to each anhydroglucose unit in cellulose in the two ways described is called “moles of substituent combine,” or (MS).

Solubility in water is achieved as the degree of substitution is increased. By selecting appropriate reaction conditions and moles of substituent, complete and quick solubility in water is obtained. HEC with an MS of 2.5 is most frequently used in latex paints because of its optimal water solubility. An idealized structure of HEC is shown in Figure 68.2.

68.3 Types and Grades of Hydroxyethylcellulose

By controlling the chain length of the cellulose backbone, HEC can be produced in a wide range of viscosity types. However, economics indicate that medium [2% Brookfield viscosity = 4500 to 6500 cPs (mPa·s at 25°C)] or higher viscosity grades are used to prevent sagging, and they can improve stability of some latex paint formulations. Most paints require 0.1 to 1% by weight of HEC to be thickened to the desired viscosity.

Hydroxyethylcellulose is also produced in a grade having superior biostability. Water is the continuous phase in latex paints. In addition, many of the components of a latex paint are manufactured in an aqueous environment. Whenever water is present, microbial growth may occur. The growth of these microorganisms is accompanied by the production of enzymes, including the cellulytic types. Cellulase enzymes break the bonds between adjacent unsubstituted anhydroglucose units in the cellulose backbone. This degradation reduces the molecular weight of the polymer, causing it to no longer be an effective thickening agent.

The process by which biostable HEC is manufactured results in a product in which the hydroxyethyl groups are distributed more uniformly along the cellulose backbone, as opposed to forming longer side chains. The more uniform distribution protects significantly more bonds from enzyme attack.

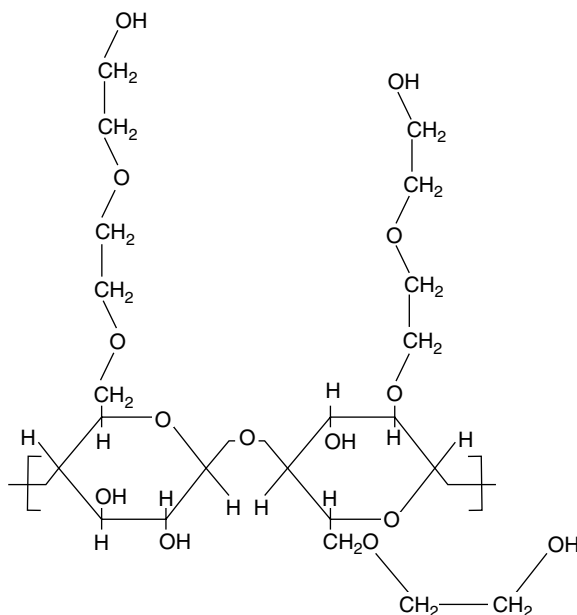


FIGURE 68.2 Idealized structure of hydroxyethylcellulose.

68.4 Chemical and Physical Properties of Hydroxyethylcellulose

Most water-soluble polymers have a tendency to lump or agglomerate during the dissolving process. When the polymer is added to water, the outer layer of the agglomerate swells to a gel very quickly, making it difficult to hydrate the inner portions. The time required for the polymer to dissolve completely is governed by the degree to which it agglomerates. To avoid agglomeration, HEC particles are surface treated with a substance, typically glyoxal, which cross-links the surface and produces a product that is temporarily insoluble in water. This temporary insolubility permits thorough dispersion of discrete particles of HEC. Once the glyoxal cross-links have been hydrolyzed by the water, the HEC will begin to dissolve without agglomerating.

Hydrolysis of the glyoxal cross-links is influenced both by temperature and pH. Figure 68.3 shows that increasing the temperature and increasing the pH both shorten the hydration time. (Hydration time is defined as the time between addition of HEC to water and the time when viscosity starts to develop.) In fact, by raising the water pH to levels of 8 and above, the hydration time is decreased so much that the surface treatment is no longer an effective means of improving dispersion.

68.5 Incorporating Hydroxyethylcellulose into Latex Paints

An important benefit of hydroxyethylcellulose for latex paint manufacturers is that it can be added to the batch at several different points. This gives the formulator process flexibility. Most often, at least some of the HEC required to thicken a batch of paint is added to the pigment grind. This increases the viscosity of the grind and makes it a more efficient dispersing medium. However, some manufacturers find it possible to achieve a good pigment dispersion in a low viscosity grind, and then add HEC later. HEC can be used in the powder form (as is), dissolved in water, or slurried in a nonsolvent before addition to ensure that a gel-free paint is manufactured.

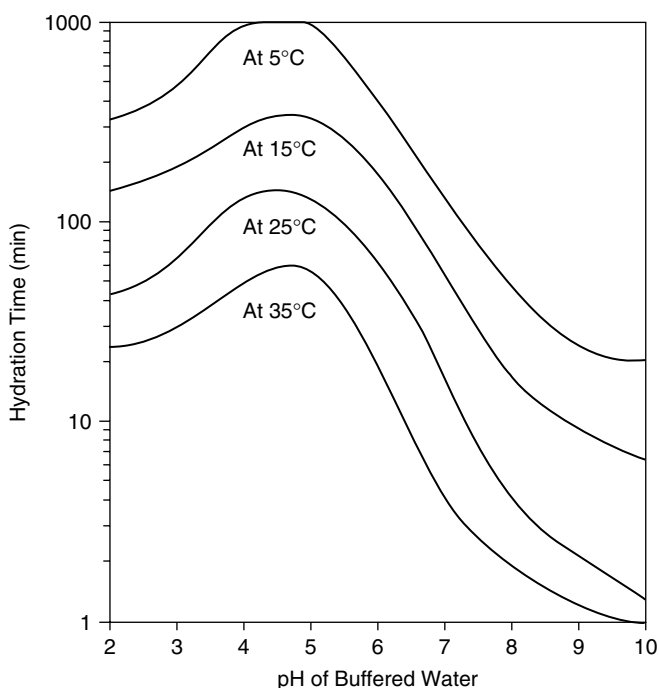


FIGURE 68.3 Effect of pH and temperature on the hydration time of HEC.

68.6 Application Properties of Latex Paints Thickened with Hydroxyethylcellulose

The primary purpose of a thickener in a latex paint system is to control rheology, or flow properties. Hydroxyethylcellulose thickeners influence the rheology primarily by thickening the aqueous phase. Fairly strong hydrogen bonds are formed between the polymer chain and water molecules. The resulting chain association forms a concentrated network. Because HEC thickens the water only, its efficiency is independent of the latex, surfactant, or dispersant type. Formulation insensitivity is the greatest benefit of HEC. Also, very little viscosity change or phase separation seen in shelf stability, heat stability, or freeze-thaw stability testing is attributable to the aqueous phase thickening mechanism. Sections 68.6.1 through 68.6.3 describe the effect of molecular weight or viscosity type of HEC on the important properties of leveling, sag resistance, film build, and spatter resistance.

68.6.1 Leveling and Sag Resistance

Very low shear rates are present in the paint during the leveling process (disappearance or reduction of brush marks in the paint immediately after application). In general, high molecular weight grades of HEC should be used if improved leveling is desired. Paint viscosity curves (Figure 68.4) show that paints with higher molecular weight thickeners have the lowest viscosities in the low shear rate region. Low shear rate viscosity data have been found to be good predictors of leveling when the only variable in a series of paints is the molecular weight of the HEC thickener. When comparing one formula with another, it is important to examine also the rate of viscosity recovery after shearing, to be able to predict leveling.

A second cause of poor leveling is wicking. When the water is adsorbed quickly into the substrate, the brush marks are frozen. To alleviate this condition, a greater amount (lower molecular weight) of HEC should be used.

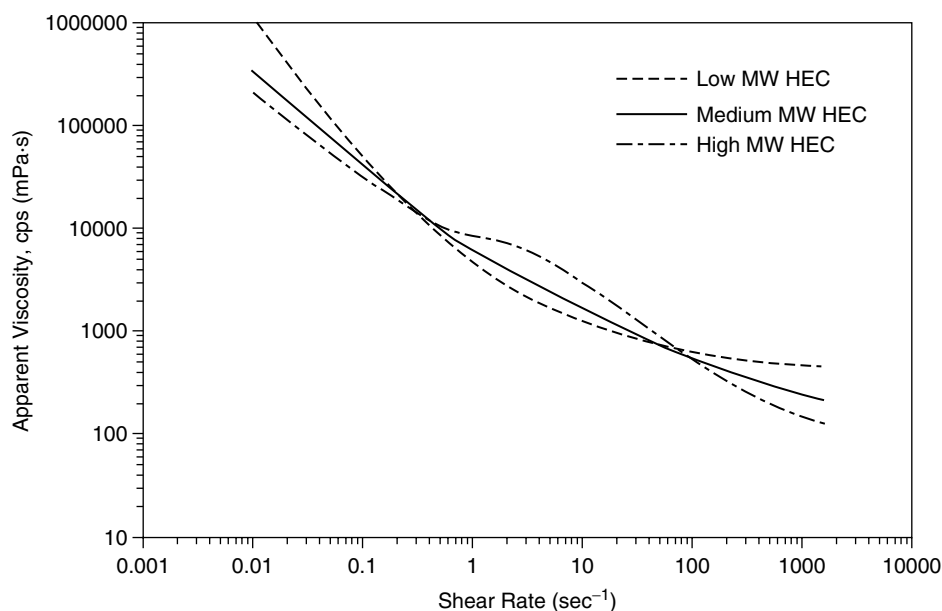


FIGURE 68.4 Influence on paint viscosities of molecular weight of HEC and shear rate.

68.6.2 Film Build

Good film build, a prerequisite for one-coat hiding, has been shown to be directly related to viscosity during the high shear processes of brush and roller application. This viscosity is controlled by thickener concentration. Therefore, to increase the film build of a formula while maintaining the Stormer viscosity, a greater amount of a low molecular weight HEC should be used.

68.6.3 Spatter Resistance

Spatter resistance, also a high shear application property, does not depend on thickener viscosity, but on the elasticity of the aqueous phase. Like film build, spatter resistance can be predicted from the polymer solution rheology. Higher molecular weight thickeners are more elastic, and consequently impart elasticity to the paint. Paint made from lower molecular weight grades of HEC is more resistant to spatter during roller application.

During roller application, threads of paint are pulled off the nip of the roller. When the thickener has some degree of elasticity, these threads are stabilized and can be stretched farther before breaking. More spatter is created when these threads are stabilized and stretched than if they break close to the nip of the roller.

Reference

1. K. G. Shaw and D. P. Leipold, *J. Coat. Technol.*, 57(727), 63–72 (1990).